Direct Fluorination of Disordered Rock Salt Cathode Oxides : Synthesis and Characterization

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Oak Ridge National Laboratory

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Overview

Timeline

- Project start date: Oct. 1, 2018
- Project end date: Sept. 30, 2021
- Percent complete: 60

Barriers

Performance

Capacity: Cathode specific capacity ≥ 250 mAh/g @ nominal voltage ≥ 3.8 V wrt Li^o/Li^+

Rate: 3C or higher

Life: Minimum 1000 deep discharge cycles

Budget

- FY19 Funding: $400K
- FY20 Funding: $450K

Partners/Collaborators

- Lawrence Berkeley National Laboratory & University of California, Berkeley
  Guoying Chen, Wei Tong, Gerd Ceder, Kristin Persson, Bryan McCloskey, Wanli Yang, Robert Kostecki– Synthesis, Modelling & Characterization

- University of California, Santa Barbara
  Raphaële Clément-NMR
- University of Tennessee
  Sheng Dai - Fluorination
- *Pacific Northwest National Laboratory*
  Chongmin Wang- Electron Microscopy

Relevance

Impact

Development of high energy density cobalt-free cathodes are critical to meet the growing demand for advanced lithium-ion cells for electric vehicles. In this context, cobalt free high capacity disordered cation rock salt (DRX) is a potential alternative to the layered NMC or NCA based cathode chemistries and can achieve energy densities up to 1000 Wh/Kg

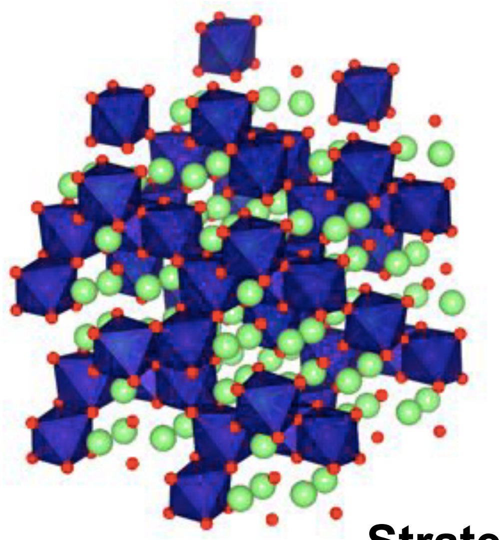
Objectives

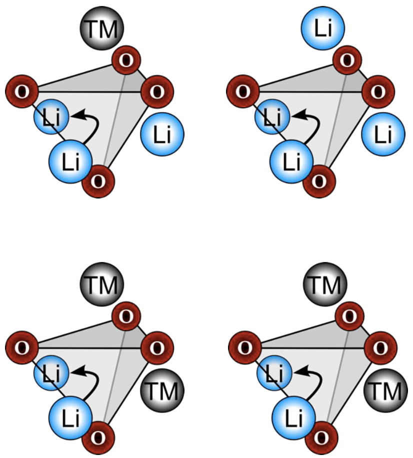
- Synthesis and electrochemical performance optimization of DRX composition based on effective charge compensation
- Undertake alternate fluorination methods for DRX compositions to achieve greater oxidative and cycling stability
- **Characterization:** Use neutron scattering, Raman, and NMR methods to understand short-range and long-range structure and correlate with lithium transport

Relevance to VTO Mission

Address VTO programmatic goals of understanding and mitigating existing materials issues that prevent *state-of-the-art* Li-ion battery systems from achieving higher practical energy densities, lower cost, safer performance, better lifetimes, and less reliance on security critical materials

Cation disorder rock salt cathodes are a class cobalt free cathodes that provide an effective design framework to achieve high capacity and high voltage stability by cation and anion co-substitution





Cation disorder rock salt structures allow different Li coordination or bonding environments unlike layered cubic cathodes

At > 10 % Li-excess 0-TM channels form a percolative pathway for lithium diffusion

Strategy

- Lower the redox active TM (such as Mn) by high valent substitution – Nb^{5+}, Ti^{4+} Mo^{6+} that are d^0 transition metal configuration
- Lower the anionic charge by replacing O^{2-} with F^{-1}
- Optimize F-solubility in DRX tuning the synthesis method

Effective charge compensation to maximize capacity

Composition	TM Cations
$Li_{1+x}V_2O_5$	V^{3+}, V^{5+}
$LiM_{0.5}Ti_{0.5}O_2$ (M = Fe, Ni)	M^{2+}, Ti^{4+}
$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$	Mo^{5+}, Cr^{3+}
$Li_{1.3}Nb_{0.3+x}M_{0.4-x}O_2$ (M = Mn, Fe, Co, Ni)	Nb^{5+}, M^{3+}
$Li_{1.6-4x}Mo_{0.4-x}Ni_{5x}O_2$	Mo^{6+}, Ni^{2+}
$Li_{1.3}Nb_{0.3}V_{0.4}O_2$	Nb^{5+}, V^{3+}
$LiCo_{0.5}Zr_{0.5}O_2$	Co^{2+}, Zr^{4+}

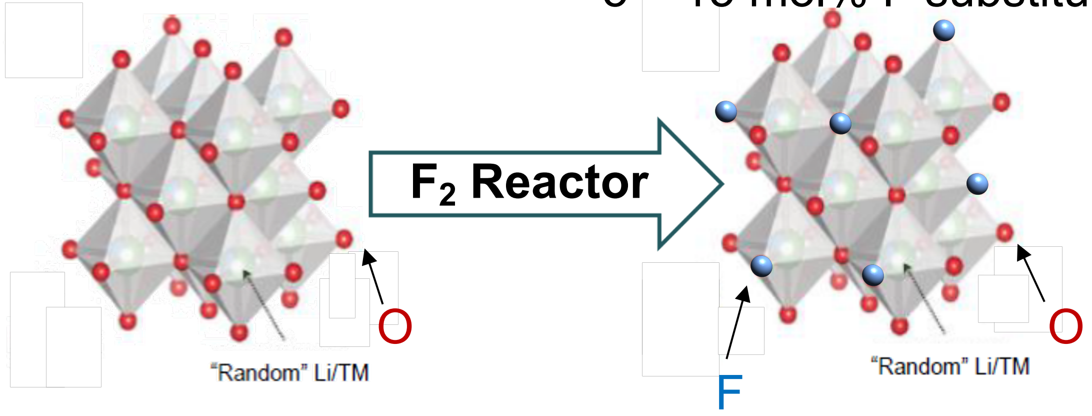
J Lee, Ceder et al., Science, 343 (6170), 519-522 (2014)

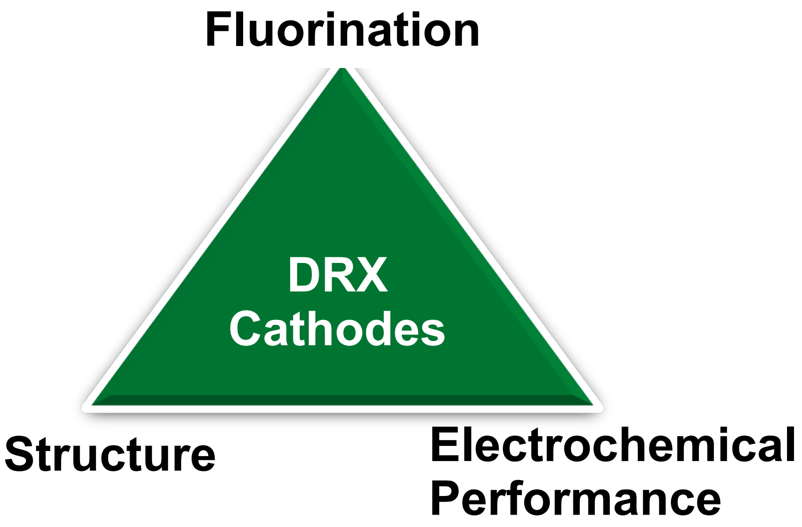
Develop alternate fluorination routes for disordered rock salt (DRX) cathodes to increase fluorine solubility

We use an *in-situ* fluorine gas reactor under controlled conditions as one of the methods to incorporate fluorine in DRX cathodes

Baseline DRX Structure

Target: 5 – 15 mol% F substitution





Compositions for investigation at ORNL from DRX deep dive team

- $Li_{1.2}Nb_{0.3}Mn_{0.5}O_2$ (LNMO)
- $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (LMNOF)
- $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (LNTMOF)
- $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ (NTMO)

ORNL Research Scope

1. Optimize the fluorinated composition for better capacity retention and stability
2. Determine limits of F-solubility and/or impurity phase formation
3. Local structural and spectroscopic characterization of DRX cathodes

Image adapted from: Lee, Ceder et al. *Energy Environ. Sci.* **8**, 3255-3265 (2015).

FY20 Milestones

Due Date	Description	Status
12/31/2019 (Q1)	Analyze the short-range order (SRO) of a few selected DRX compositions from neutron powder diffraction, microscopy, and NMR data	Complete
03/31/2020 (Q2)	Synthesize and optimize two DRX compositions using fluoride containing precursors No-Go: Stop fluorination of lithiated DRX compositions	Complete
06/30/2020 (Q3)	Undertake synthesis of two high F content DRX compositions (> 15% wt F) using direct fluorination method by adjusting the M:F ratio	In progress
09/30/2020 (Q4)	Complete electrochemical and structural characterization of fluorinated DRX composition and compare with baseline composition (unfluorinated)	In progress

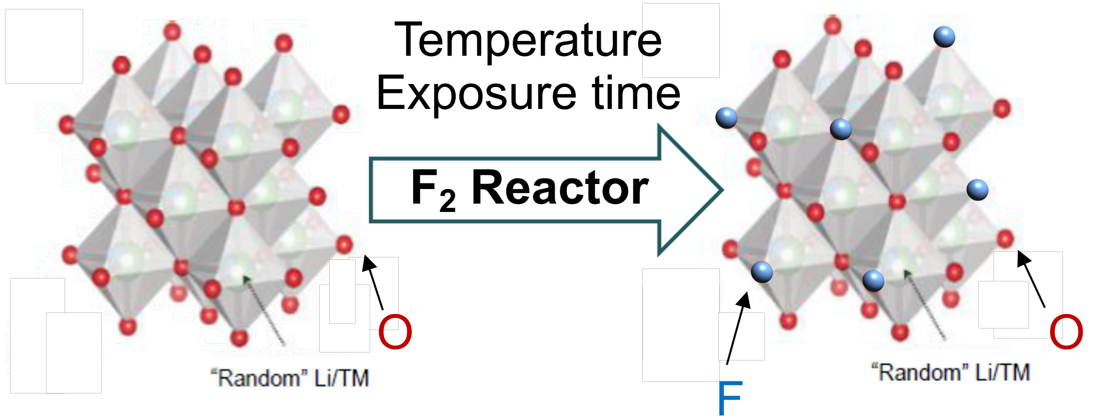
Fluorine content in several DRX cathodes was controlled by adjusting reaction temperature, time and F_2 flow rate.

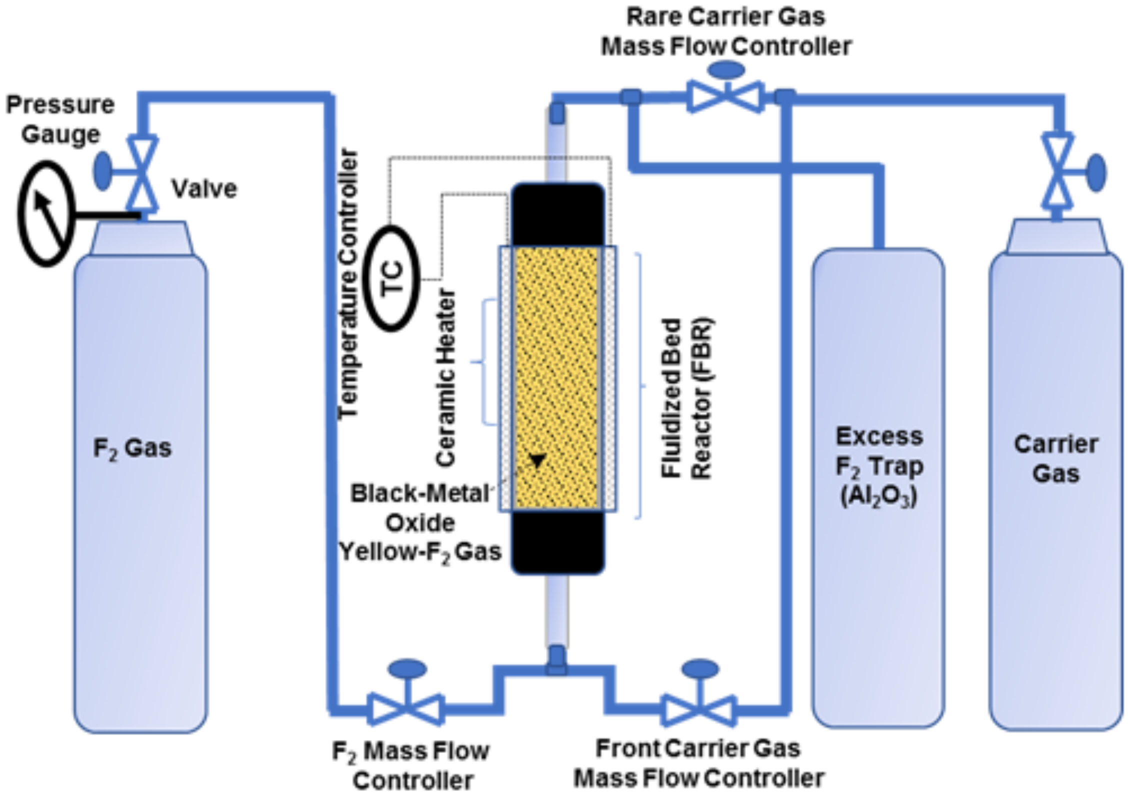
Based on modelling studies we determined the upper bound of F-solubility in each DRX composition based on lithium content and transition metal (TM) to anion (oxygen) ratio

(A) Direct fluorination of existing baseline fluorinated DRX compositions
(B) Direct fluorination of pristine DRX oxide compositions
(C) Direct fluorination of TM oxide as precursors for synthesis of DRX compositions

Compositions for direct fluorination:

- $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$ (MNOF)
- $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (LNTMOF)
- $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ (NTMO)

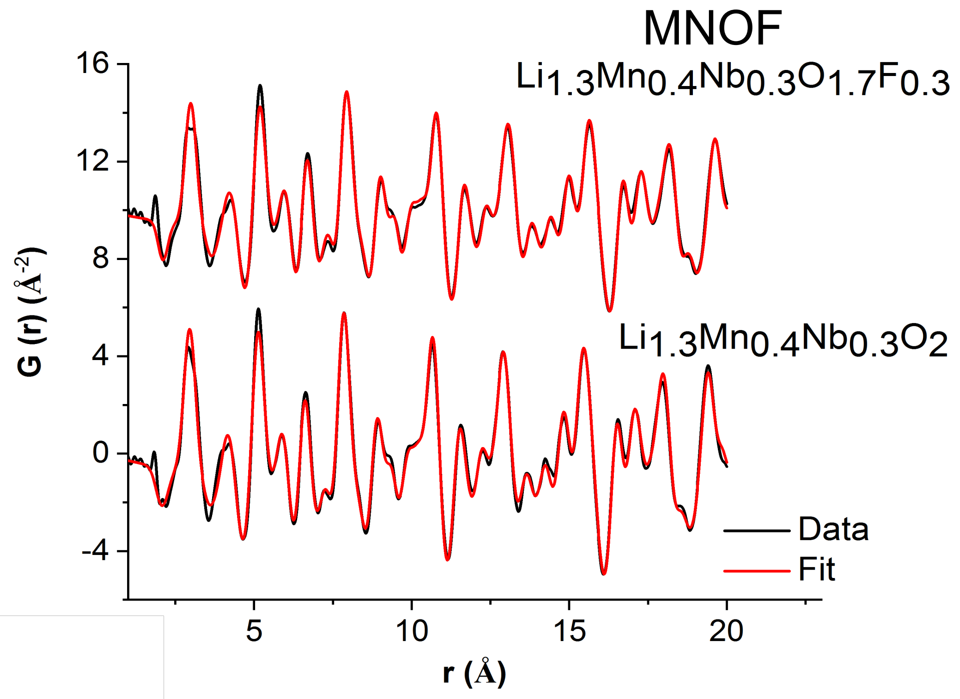


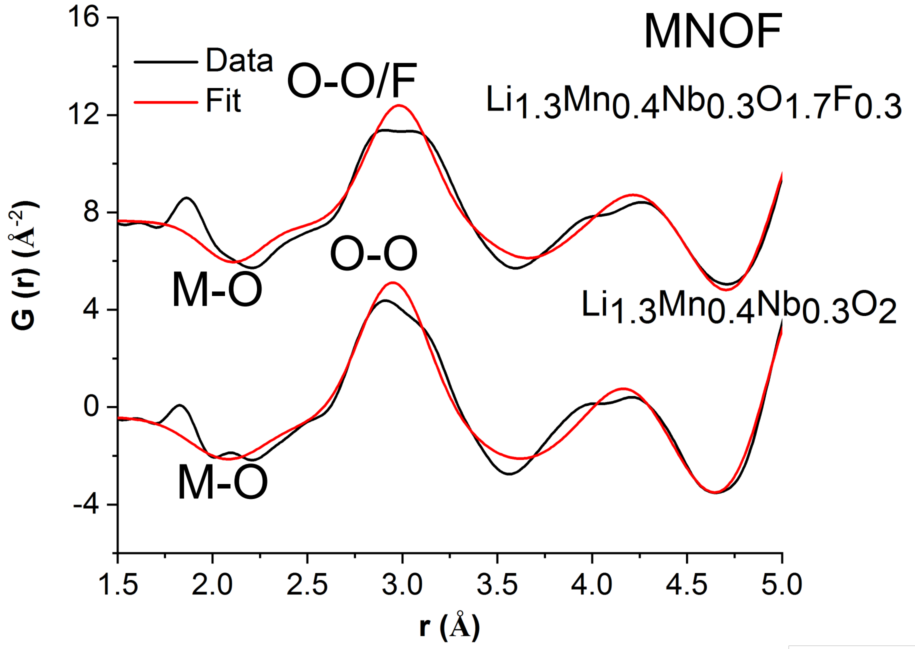


Schematic of direct fluorination reactor

Neutron Pair Distribution Function (PDF) analysis indicates MNOF cathodes exhibit local short-range ordering (< 5 Å). The local structure changes based on the fluorine content

- The long-range structure (> 5 Å) for both pristine DRX oxide and fluorinated (MNOF) fits reasonably to the disordered rock-salt structure (Fm-3m)
- Short-range ordering (< 5 Å) clearly shows (e.g., O-O peak splitting) which deviates from the randomly disordered rock-salt structure
- Short range ordering (SRO) changes with fluorine content and could play a role in lithium transport

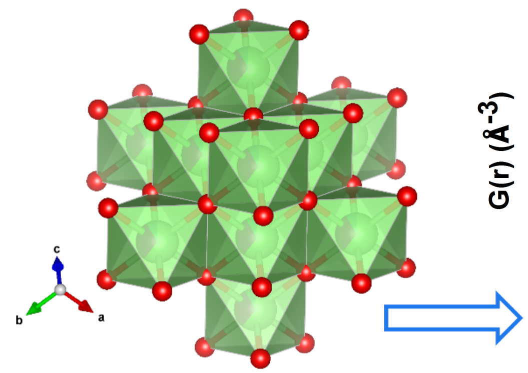


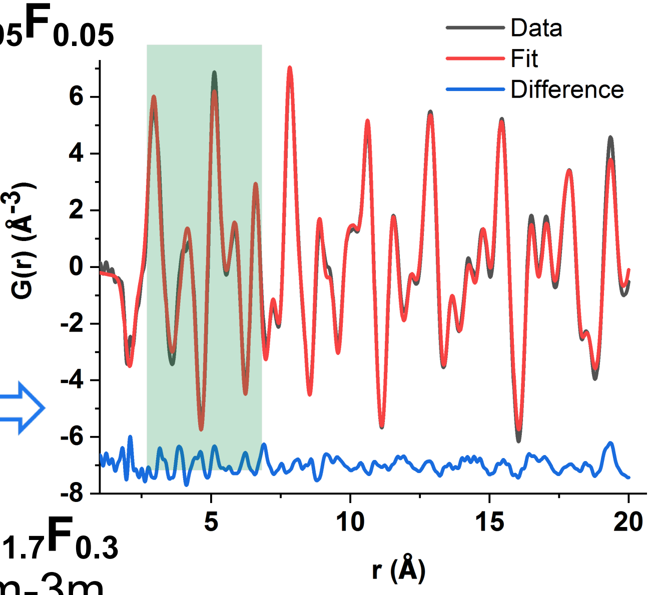


J. Liu –ORNL and B. Ouyang- LBL

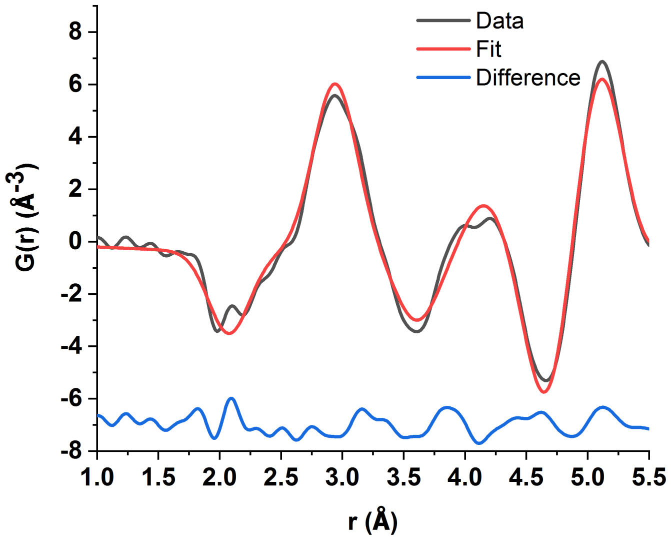
Short range order (SRO) as determined from neutron PDF show a different local structure for DRX which could play a role in lithium transport

$Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$

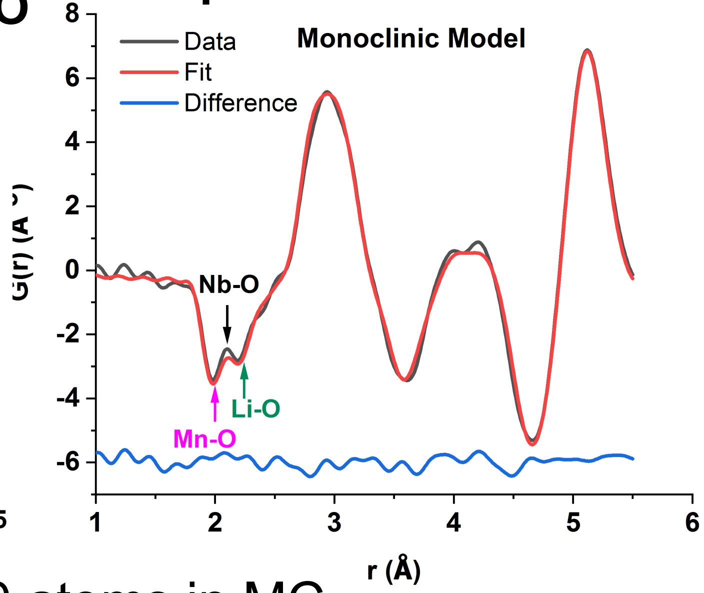




Does not fit the local SRO

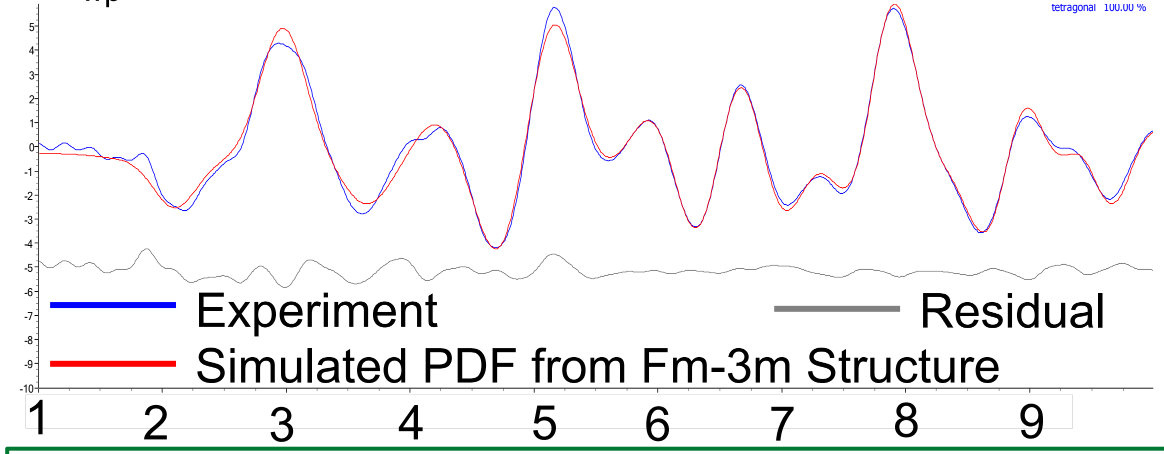


Captures the SRO well

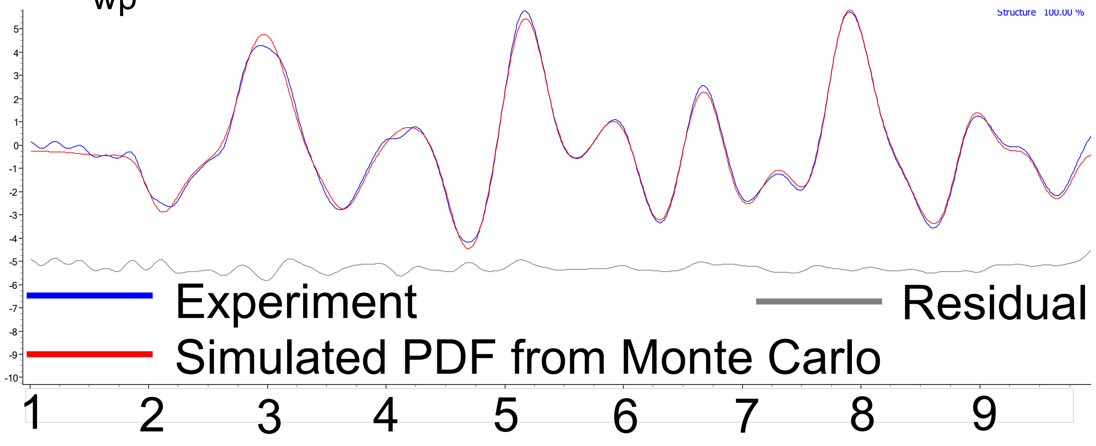


$Li_{1.3}Mn_{0.4}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$

R_{wp} = 11.7% from Fm-3m



R_{wp} = 9.01% from 160 atoms in MC



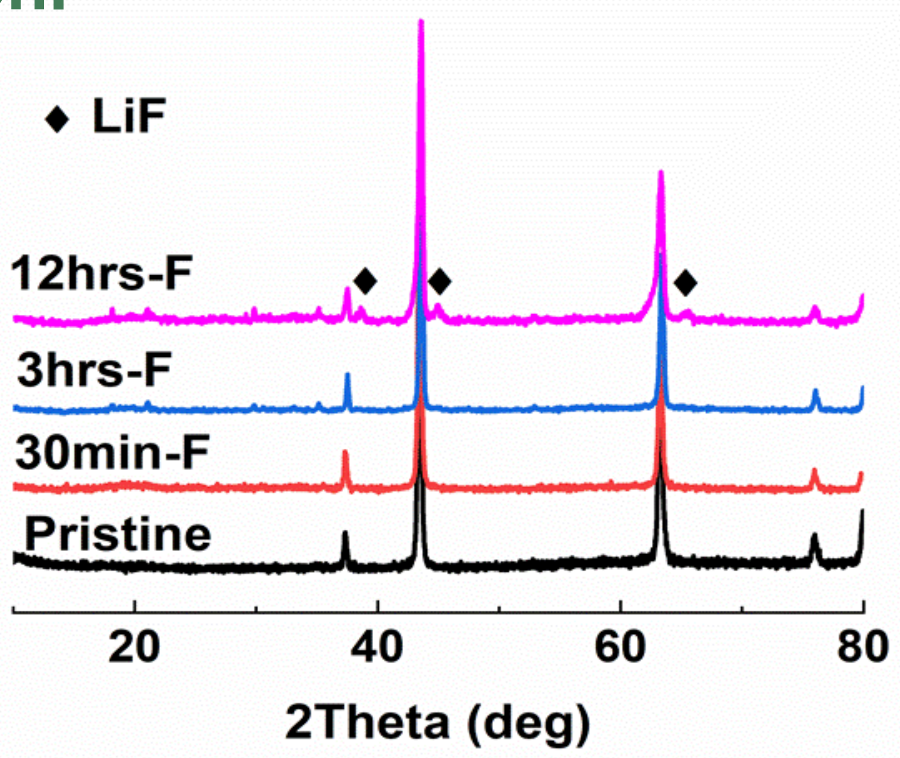
Key Findings

- Fm-3m fit well in long range order. Monoclinic model fit well for SRO below 6 Å in $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
- 160 atoms in Monte-Carlo simulation fit for $Li_{1.3}Mn_{0.4}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$ is better J. Liu –ORNL and B. Ouyang- LBL

Direct fluorination of $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ (NTMO) DRX cathode results in LiF formation.

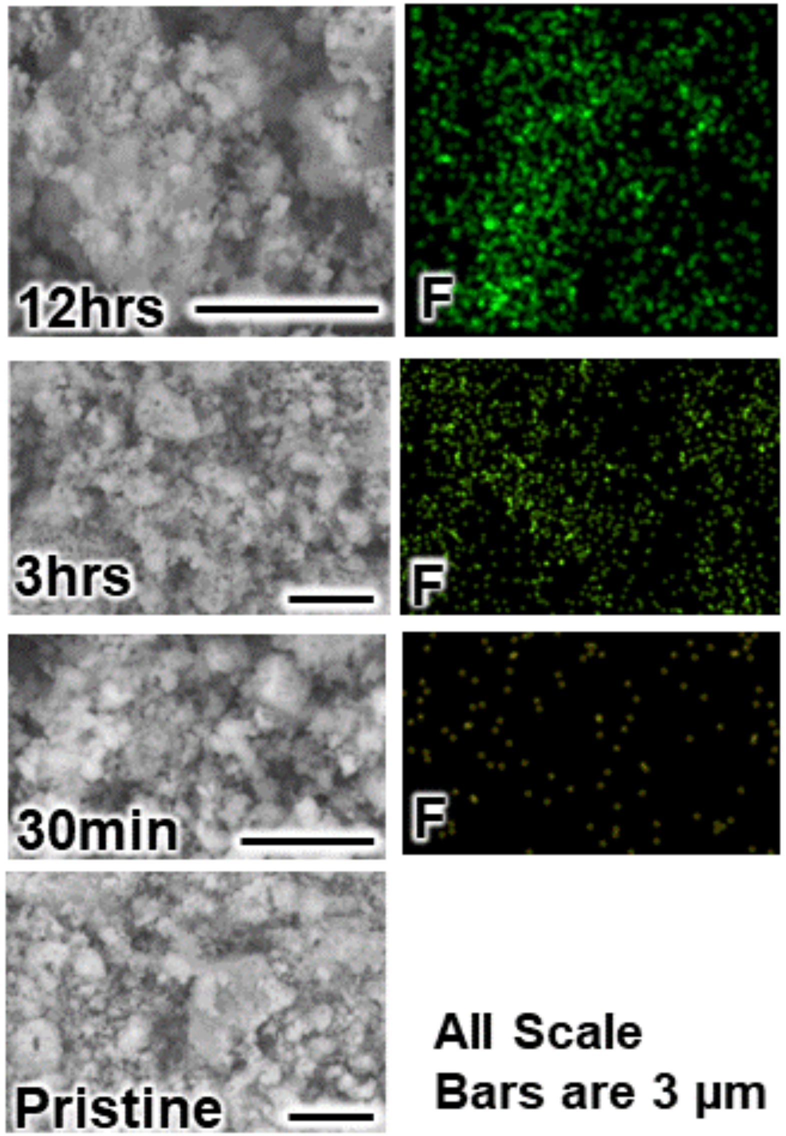
Key Findings

- The DRX bulk structure did not change after direct fluorination
- F content increased with more aggressive reaction conditions as expected.
- Crystalline LiF was detected after 12 h fluorination reaction
- Mild fluorination conditions likely lead to formation of an amorphous LiF phase

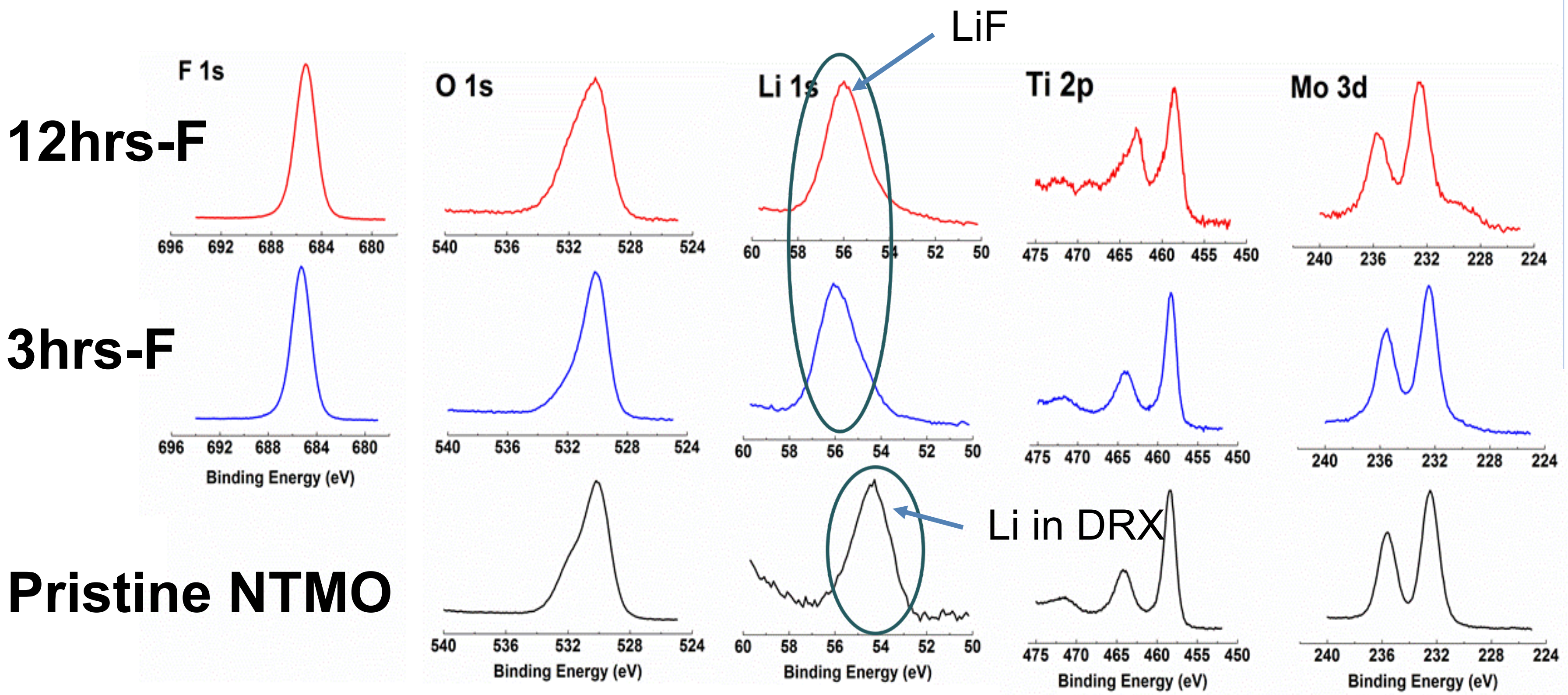


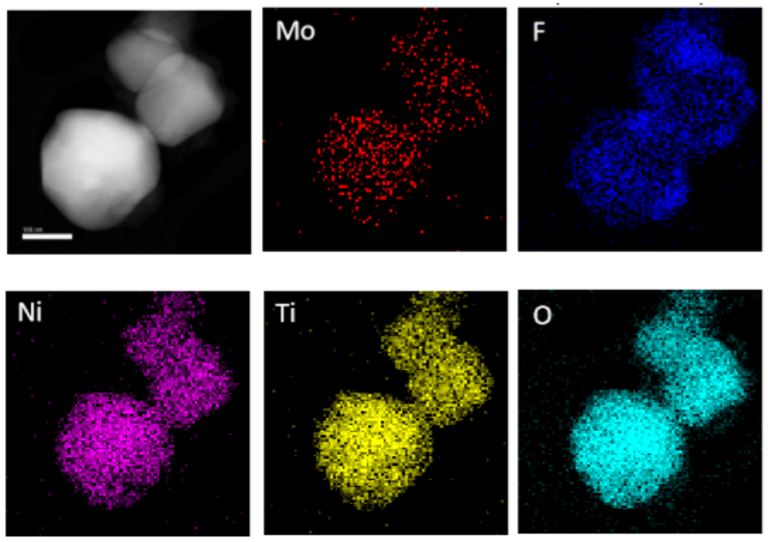
$Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ (NTMO)

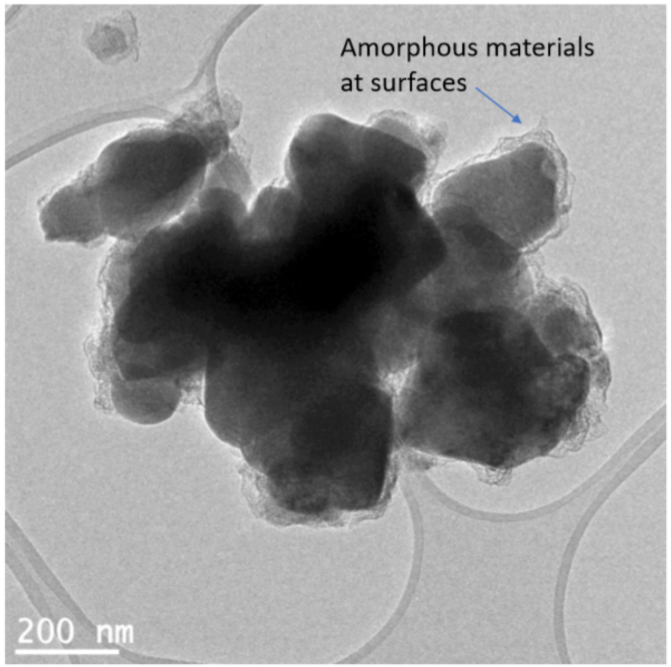
Sample	Time	T (°C)	Flow Rate (sccm)
NTMO	0	NA	NA
30min-F	30min	145	1.6
3hrs-F	3hrs	180	3
12hrs-F	12hrs	180	3



Presence of LiF surface films on fluorinated NTMO cathodes was confirmed using TEM and XPS.



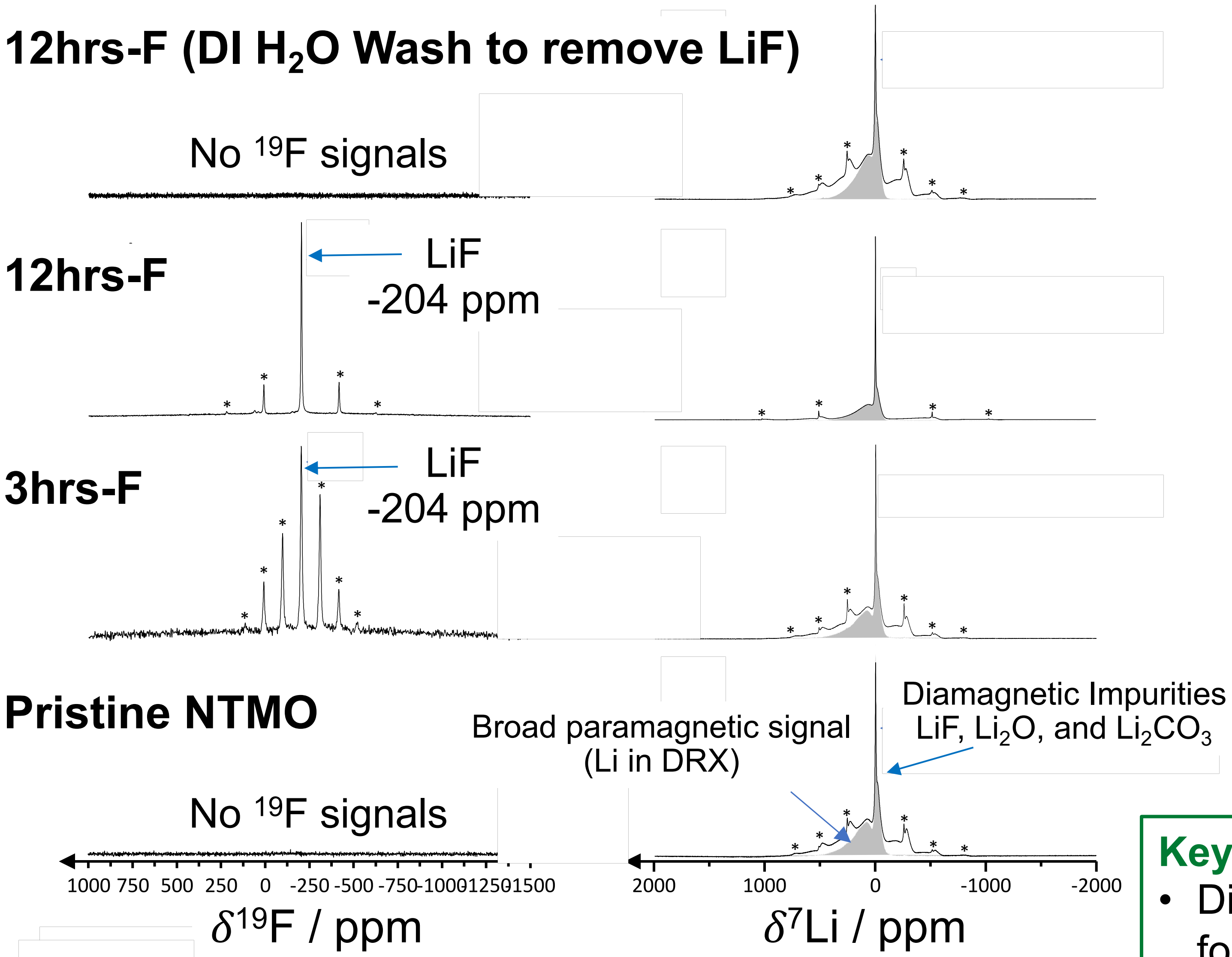




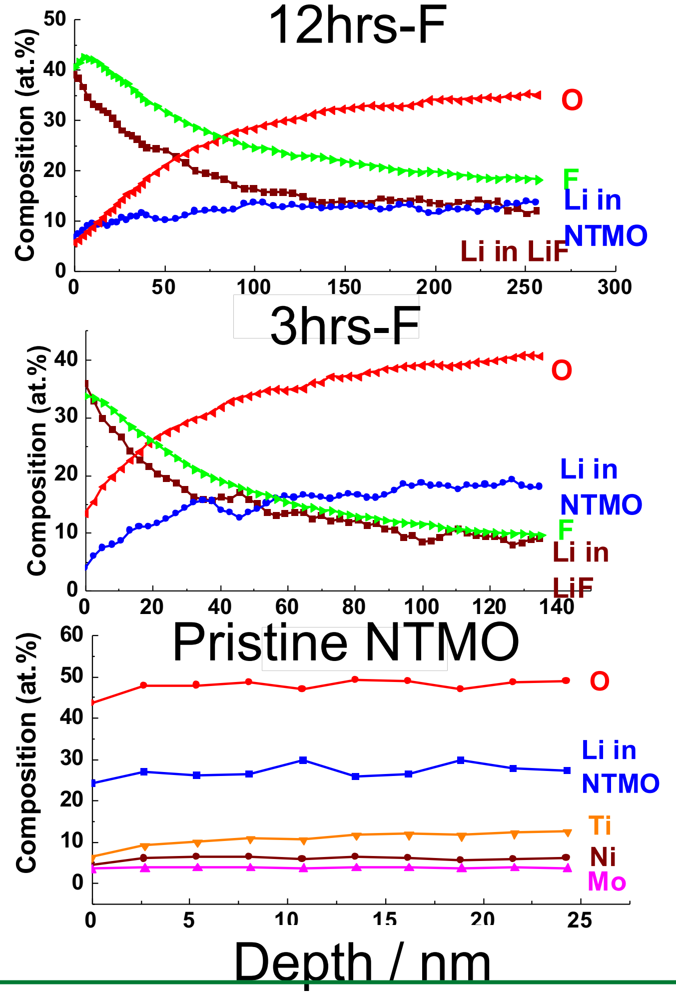
Key Findings

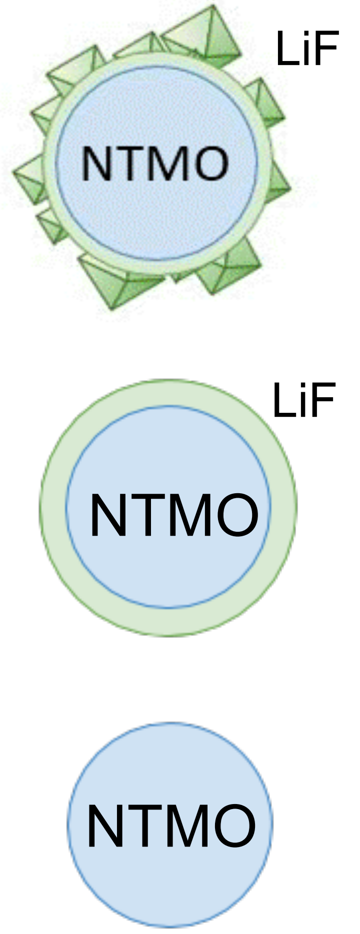
- Fluorinated NTMO contained thick LiF surface film
- Direct fluorination did not impact transition metal bonding environment
- Microscopy results showed amorphous F-rich surface

$^{19}F/^{7}Li$ NMR and XPS depth profiling measurements provide complementary information on bulk structure and surface chemistry of fluorinated NTMO.



* Spinning sidebands

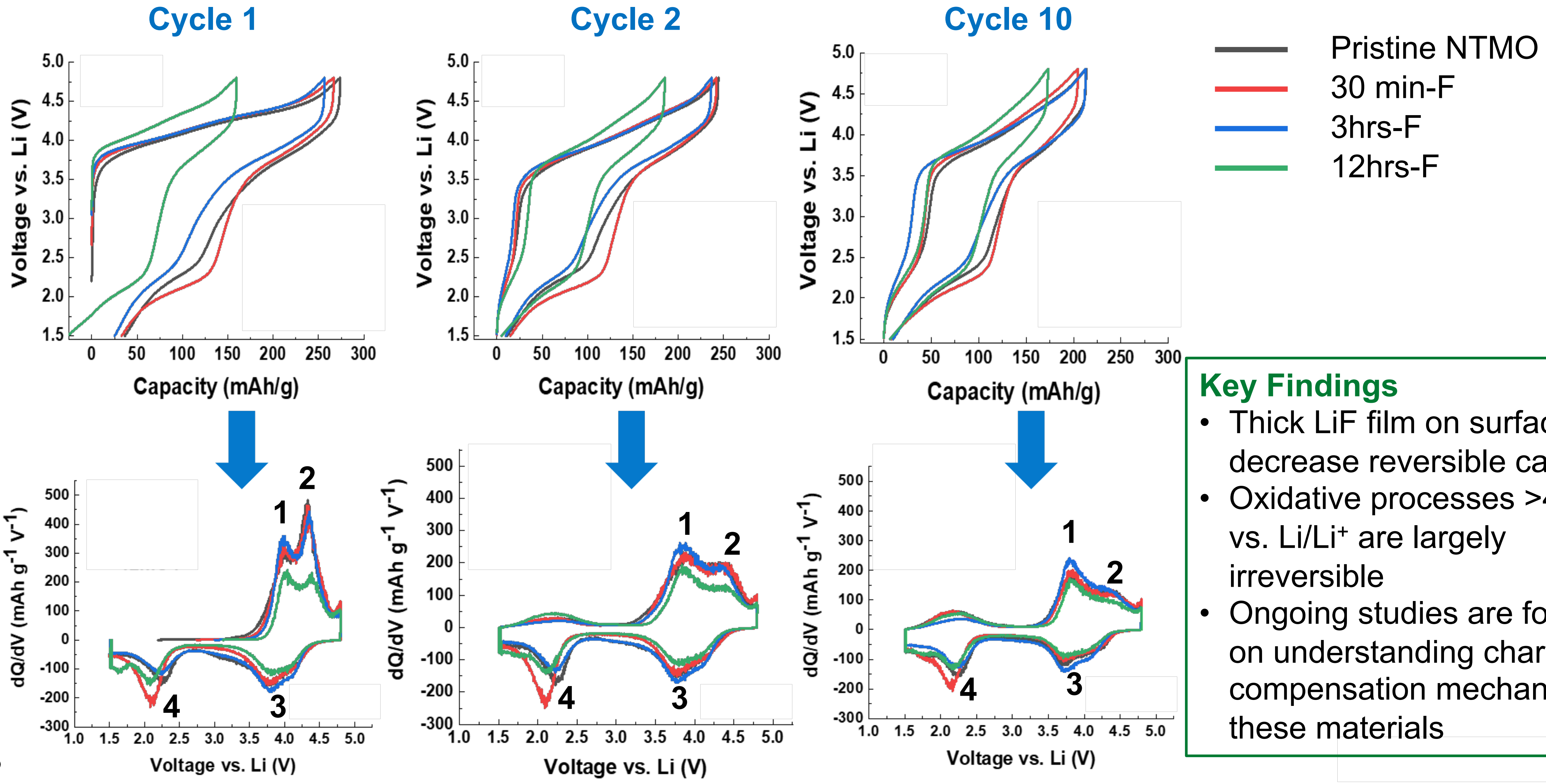




Key Findings

- Direct fluorination does not lead to F^- substitution for O^{2-} anions in DRX structure
- LiF surface film of F-NTMO is 100+ nm thick

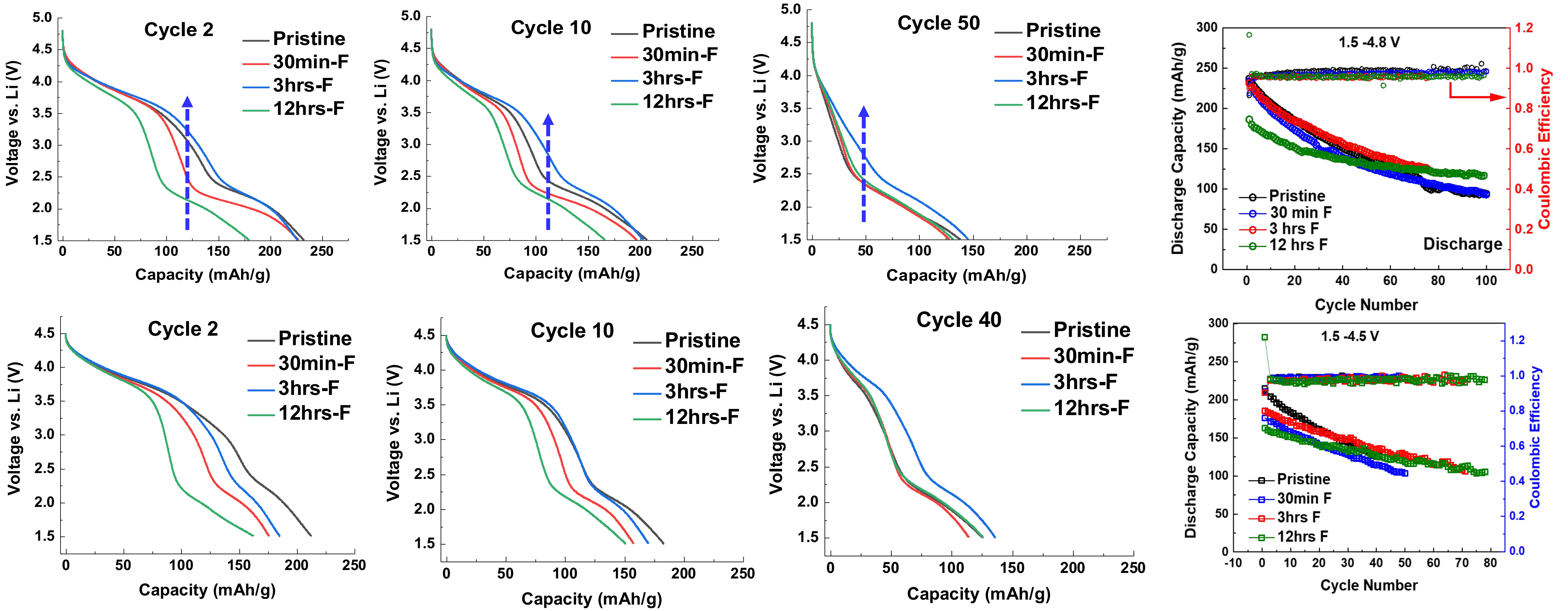
Effects of direct fluorination on electrochemical properties of NTMO cathodes were investigated. Thick LiF surface films are detrimental to DRX performance.



Key Findings

- Thick LiF film on surface decrease reversible capacity
- Oxidative processes >4.5V vs. Li/Li$^+$ are largely irreversible
- Ongoing studies are focused on understanding charge compensation mechanism in these materials

Direct fluorination reaction conditions were optimized to slightly improve cycling stability and discharge voltage of NTMO DRX cathode.



Key Findings

- Aggressive fluorination conditions (12 hrs) led to poor performance caused by thick LiF surface film
- 3hrs-F cathode exhibited improved capacity retention and higher discharge voltage compared to pristine NTMO.

Direct fluorination of pre-fluorinated DRX cathodes exhibited poor performance - No-Go

MNOF Particles:

- $Li_{1.2}Mn_{0.625}Nb_{0.175}O_{1.95}F_{0.05}$
- Y. Yue and W. Tong, LBNL

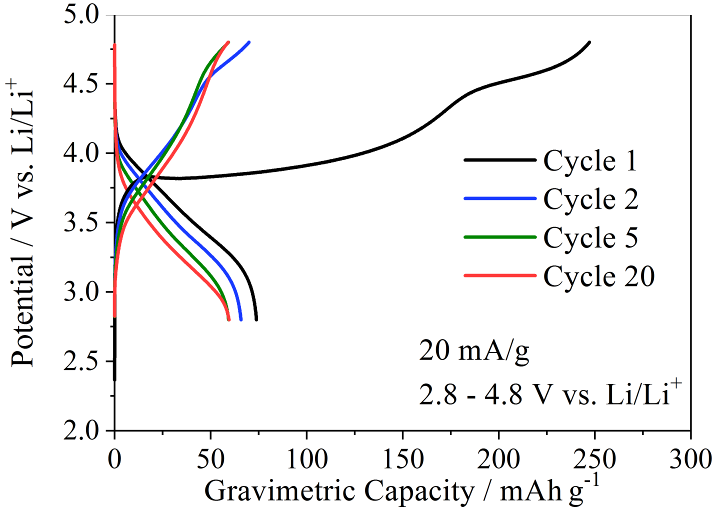
Fluorination Conditions:

- **Mild**: 100 °C, 1 h, 1.6 sccm F_2
- **Moderate**: 150 °C, 1.5 h, 1.6 sccm F_2

MNOF Sample	F Content* (at%)
Unmodified	4
Mild Fluorination	6
Moderate Fluorination	8

* from EDX analysis of Mn, Nb, O, F signals

Unmodified MNOF



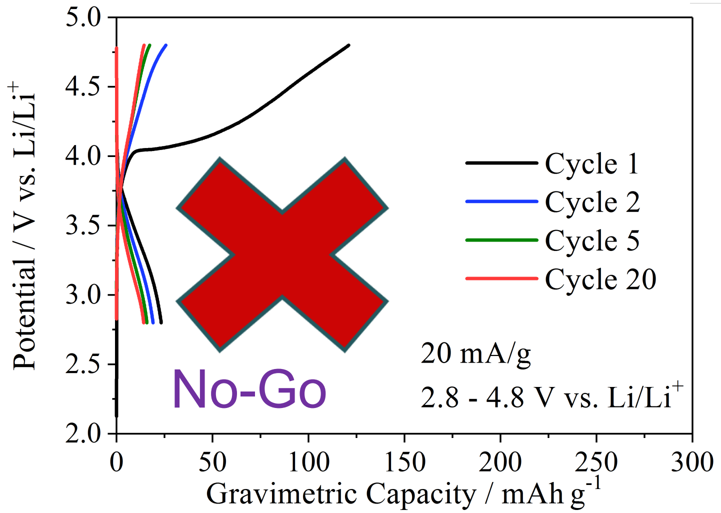
Proposed Explanations for Poor Performance

- Excess F^- amount altered the TM/O-F ratio, affecting charge compensation
- LiF formation after direct fluorination led to resistive cathode/electrolyte interface

Mitigation Strategies

- Revisit new compositions with targeted F-solubility with altered TM/O and Li content
- Develop methods to remove excess LiF and revisit the F content and electrochemical performance

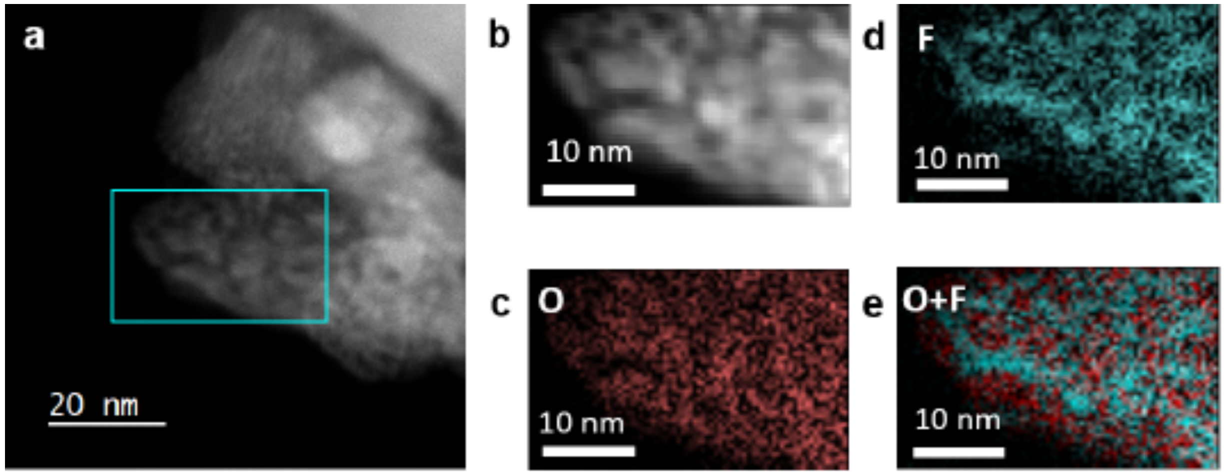
Over-fluorinated MNOF

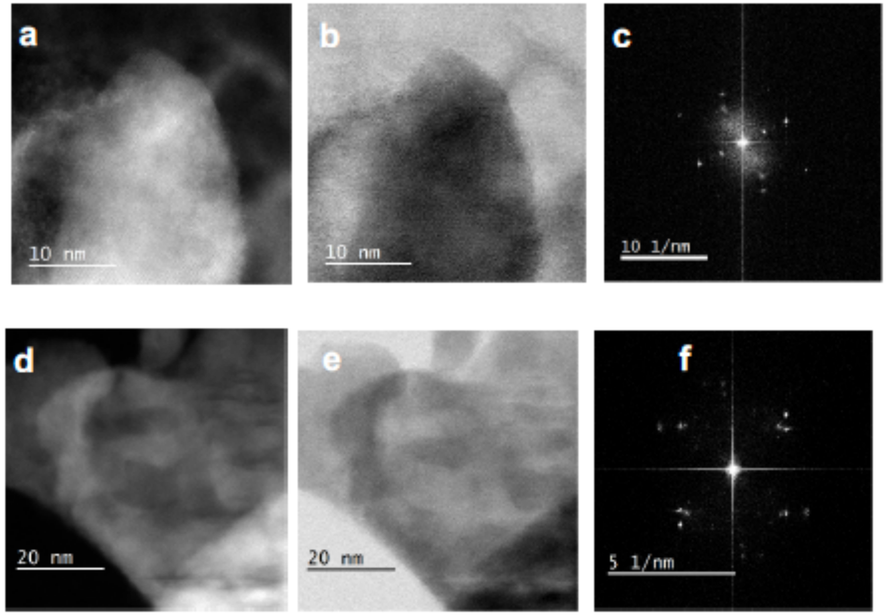


Direct fluorination of DRX composition results in LiF surface film rather than intended oxyfluorides. As an alternative strategy, we used this approach for synthesizing fluorinated precursors for DRX cathodes.

Direct Fluorination of Molybdenum Oxide (MoO_2)

Temperature	F_2 Flow rate	Time
180ºC	1.4 SCCM	12 hrs.
145ºC	1.4 SCCM	9 hrs.

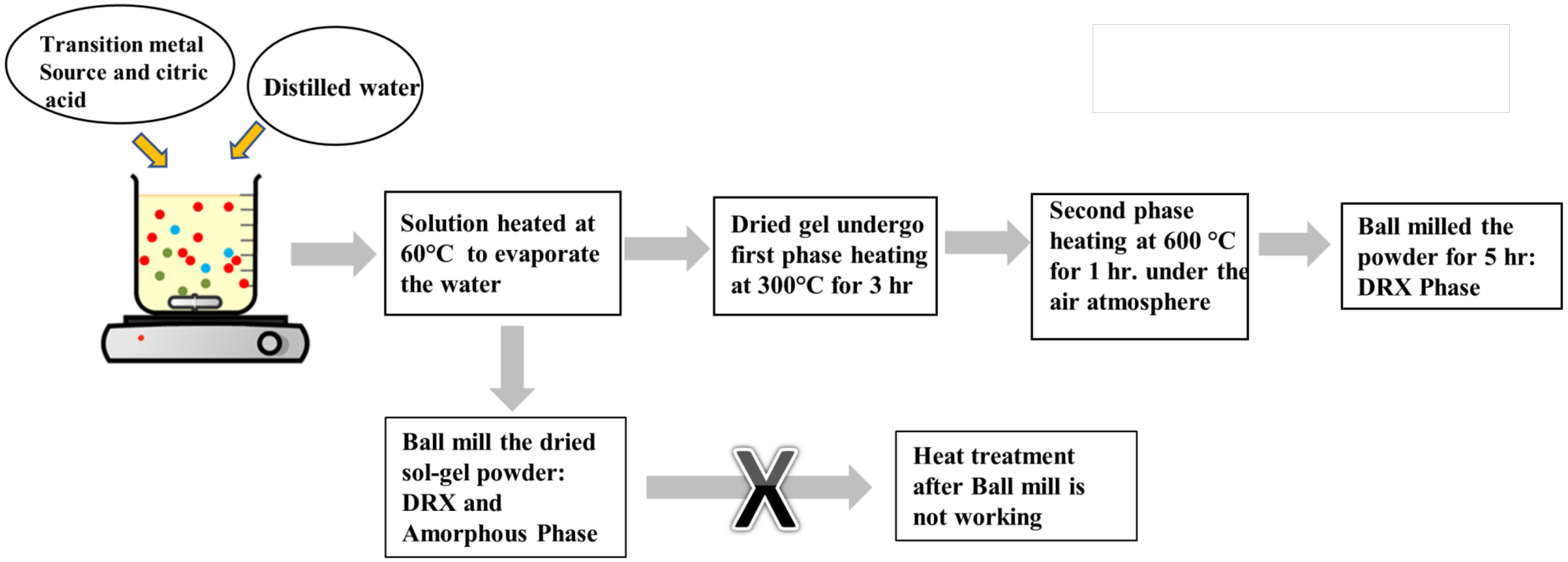




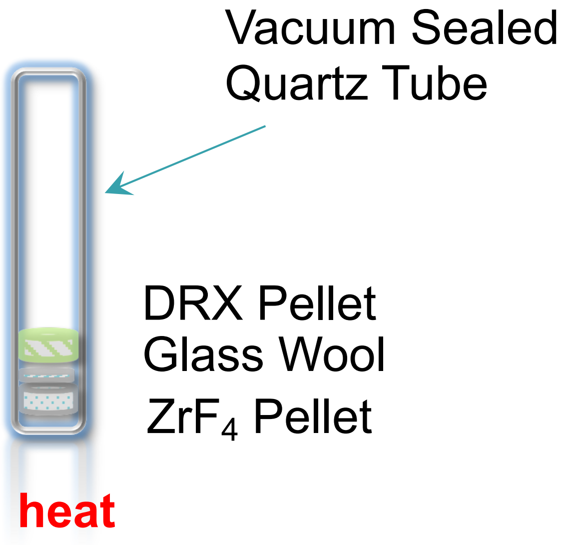
1. Direct fluorination of MoO_2 resulted in formation of mixed oxyfluoride phases - MoO_2F_2, $MoOF_4$, $Mo_4O_{11.2}F_{0.8}$ as revealed from electron microscopy and EELS.
2. Fluorinated precursors provide new method to incorporate F in DRX cathodes

New synthesis routes are being developed for oxide/oxyfluoride DRX cathodes

Method 1: Sol-Gel Synthesis Route



Method 2: Fluorination of DRX oxides via ZrF_4



Advantages of Sol-Gel vs. Solid-State Routes

- Improved mixing of TM atoms in precursor
- Lower temperature route
- Smaller particle size

Target Compound	Sol-Gel Precursors
$Li_{1.15}Ni^{2+}{}_{0.47}Nb^{5+}{}_{0.38}O_2$	$Li(OAc) + Ni(OAc)_2 + (C_4H_4N)\ NbO_9 + C_6H_8O_7$
$Li_{1.15}Mn^{3+}{}_{0.7}Nb^{5+}{}_{0.15}O_2$	$Li(OAc) + Mn(OAc)_2 + (C_4H_4N)\ NbO_9 + C_6H_8O_7$

Work in progress Q3&4 milestones

Response to Reviewers Comments

This project was not reviewed in 2019

Collaborations and Coordination with DRX Deep Dive Members

DRX Cathode Synthesis and Modelling

Guoying Chen, Wei Tong, Gerd Ceder, Kristin Persson

Bryan McCloskey (**DEMS**)
Wanli Yang (**ALS- RIXS**)
Robert Kostecki (**Interfaces**)

NMR Studies on DRX

Raphaële Clément

Electron Microscopy

Chongmin Wang

Fluorination Studies

Sheng Dai

Neutron Characterization

Jue Liu

Remaining Barriers and Challenges

- **Direct Fluorination:** Use this method for synthesizing new fluorine containing precursors for DRX cathodes
- Direct fluorination results in formation of nanocrystalline and/or amorphous domains (e.g., LiF, NiF_2) which are difficult to analyze via NMR and diffraction.
- **Morphology Control:** Mechano-chemical synthesis of DRX results in large inhomogeneity in particle sizes and shapes. Morphology control is important for higher capacity utilization and rate performance
- **Lithium Loss:** High temperature fluorination (> 900ºC) using LiF as fluoride precursor leads to lithium loss and large particle sizes. Need to find other fluorine-based precursors.
- **Estimating True F-Content in DRX:** DRX compositions have both crystalline and amorphous fluorine containing phases which makes it difficult to estimate F as part of the cathode structure versus impurities within the bulk or surface.

Any proposed future work is subject to change based on funding levels

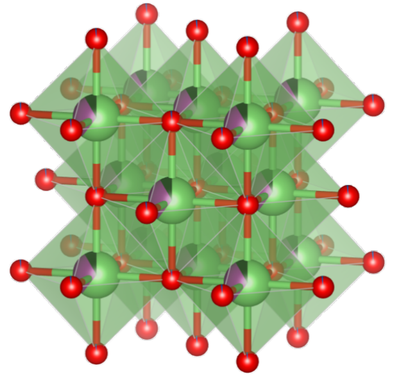
Proposed Future Research

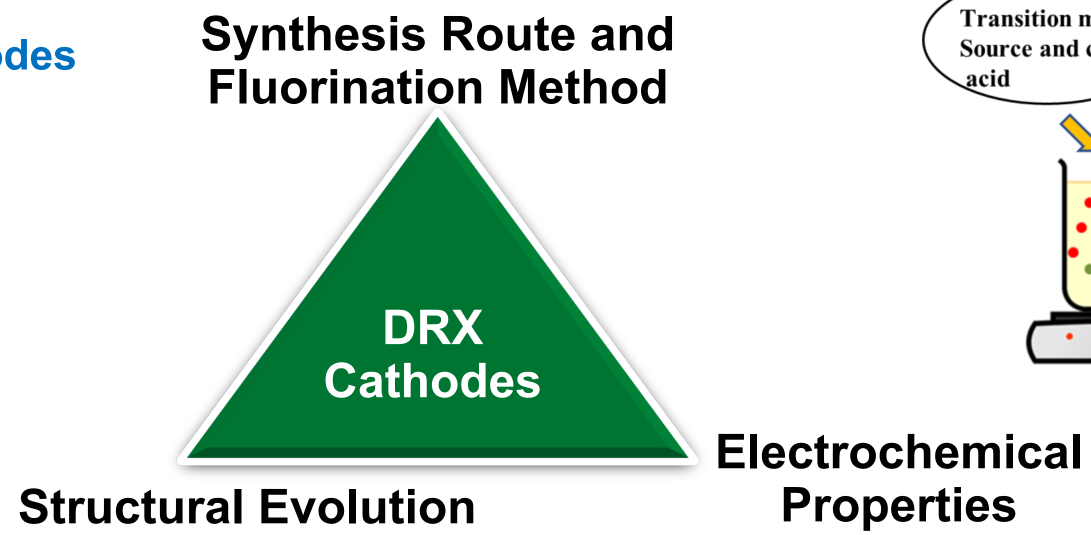
1. Develop **alternate synthesis methods** to produce DRX cathodes. Methods to be explored include sol-gel, molten salts, and co-precipitation routes. Experiments will investigate how different synthesis rotes affect the DRX capacity and rate performance.

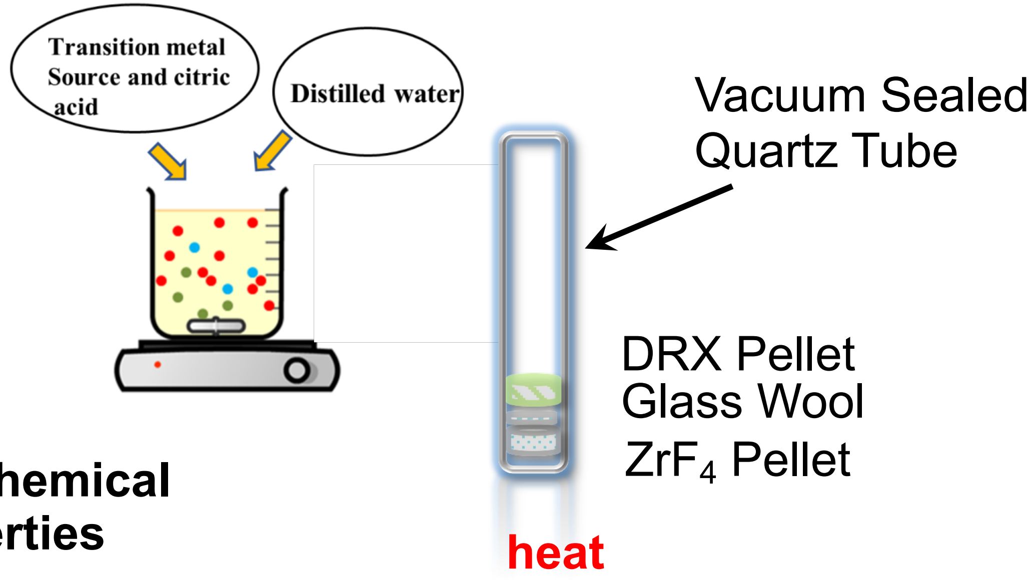
2. **Electrochemical Fluorination:** Use fluorine-containing salts and electrolytes mixtures to convert DRX oxide phase to oxyfluorides.

3. **Fluorine Solubility:** Evaluate how different fluorine precursors and synthesis routes affect F^- solubility in DRX compositions.

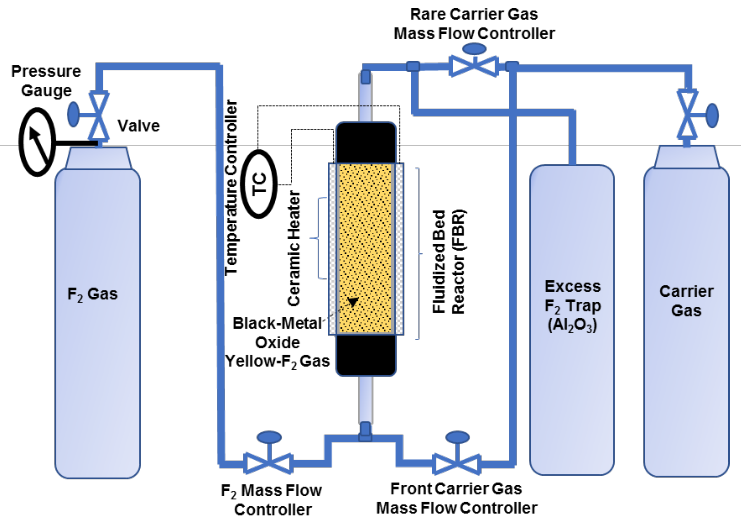
Fluorinated DRX Cathodes







Summary



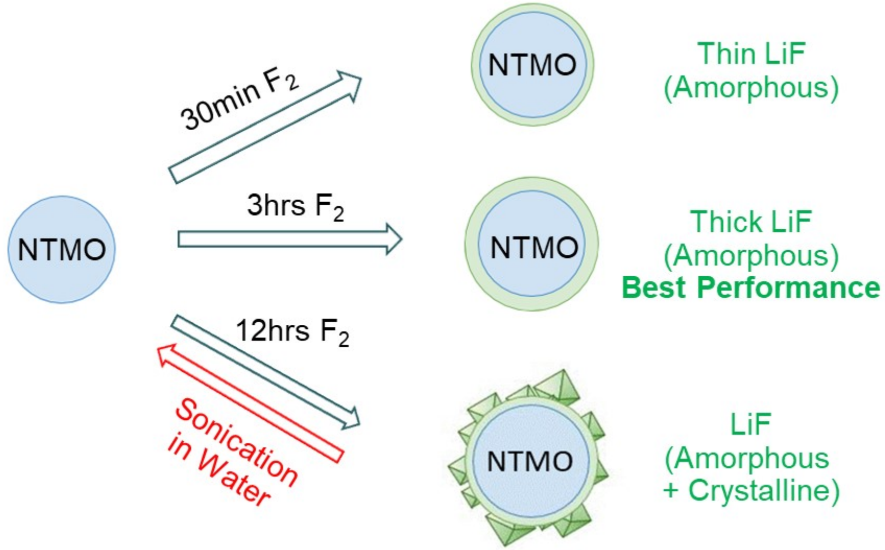
Technical Approach:

Substitute F^- into anion lattice of disordered rocksalt (DRX) cathodes using F_2 reactor

- Emphasis is placed on understanding how F substitution affects DRX structure and electrochemical performance
- Diagnostic tools include neutron scattering, microscopy, NMR and vibrational spectroscopy

Accomplishments:

- Both amorphous and crystalline LiF are formed via in-situ direct F_2 (g) reaction on $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ DRX
- Assessed local chemistry and bonding environments of fluorinated DRX cathodes using a suite of methods including NMR, TEM, and XPS
- Effects of different fluorination conditions on cathode's electrochemical properties were evaluated
- New synthesis routes were developed to produce metal oxyfluoride precursors for DRX cathodes



Ongoing work:

- Optimize F_2 reactor conditions for oxyfluoride precursors
- Develop model to describe short-range cation/anion ordering in DRX cathodes
- Develop low-T approach to synthesize the DRX cathodes with controlled morphology
- Explore new fluorination methods (e.g., ZrF_4 reagent and electrochemical fluorination)